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R110/R147

# Polymerization of styrene and.

agents (without metals of variable valency). Monoethanolamine, diethanolamine (II), sodium bisulfite, and the bisulfite compound of acetone were investigated as initiators. Their effect was investigated with systems containing different initiating activity and two complex compounds ofivalent iron. The ratio hydrocarbons (70 % by weight of styrene, 30 % by weight of butadiene) water was 1:1. 2-6 % by weight of emulsifier (Khal, Mersolate) were used. Optimum rate of polymerization was established at 0.34 % by weight of HP I and 0.2 % by weight of HP II (related to monomer). At the copolymerization butadiene-styrene by means of HP I + III, the optimum rate of polymerization was established for  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  and  $\text{Na}_2\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O} = 0.75:1$ . Increase of the concentration of III from 0.35 to 0.40 moles/mole of HP I accelerates the process considerably. After 4 hr, the polymer yield increases to ~48 % at an increase of III from 0.2-0.35 moles/mole of hydrogen peroxide, and to 65 % at a further increase. At 50°C, additional reducing agents hardly affect the rate of polymerization. At 20°C, addition of V to I + III causes polymerization acceleration and 75 % monomer conversion after 5 hr, which is only 40 % without V. In the system II and III, optimum polymer yield is achieved at 1.5 moles of III per mole of HP II. For IV, an optimum yield

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is achieved after 4 hr at a ratio 0.5 IV to I. The high rate of polymerization for systems with III is caused by the low solubility of III in water. The redox potential of III is +200 mv. In dissolved state, it reacts with  $\text{H}_2\text{O}_2$ , but it reacts only slowly. This causes the great depth of conversion. IV with high positive potential (+40 mv) is soluble in water. The rate of initiating is determined by interaction of IV with  $\text{H}_2\text{O}_2$ . Polymerization is not initiated during the unproductive reaction of III soluble  $\text{NaHCO}_3$  and well soluble HP I.  $\text{NaHSO}_3$  and poorly soluble HP II initiate polymerization. The effect of IV on III at 30°C consists

SP II initiate polymerizations. The effect of the concentration of the monomer on the rate of polymerization was studied. The results are shown in Table I. The rate of polymerization increases with increasing monomer concentration. The effect of the concentration of the initiator on the rate of polymerization was also studied. The results are shown in Table II. The rate of polymerization increases with increasing initiator concentration. The effect of the temperature on the rate of polymerization was also studied. The results are shown in Table III. The rate of polymerization increases with increasing temperature.

S. 120 5 001 012 006 0 1  
B 010B C

AUTHORS: Bereznoi, G. D. Khomikovskiy, P. M. Medvedev, S. S.

TITLE: Study of the emulsion (water) polymerization of styrene

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1969, No. 1, p. 839-845

TEXT: The polymerization of styrene is studied in emulsion stage 1-1 with the emulsifier MK (MK) - a mixture of  $C_{12}$  to  $C_{18}$  alkyl sulfonates with the average composition  $C_{16}H_{33}SO_3Na$  and sodium laurate (SL). Polymerization was initiated by potassium persulfate (PPS), azobisisobutyronitrile (DN) and benzoyl peroxide (BP). The methods used to determine the polymerization rate ( $v$ ) and the mean polymerization degree ( $\bar{P}_n$ ) had been described by the authors in Ref. 1 (Vysokomolekulyarnyye soyedineniya, 1969). All polymerization experiments were performed at 50°C, using a volume ratio of monomer to emulsifier solution of 1:1. The polymerization rate is given in grams of polymer per 100 ml. of aqueous phase per minute. The

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Study of the emulsion (later)

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B124/B101

with increasing emulsifier concentration, and does not vary with the conversion degree provided the emulsifier concentration is kept constant. Assuming that termination takes place by the interaction of two polymer radicals, the equation  $P_n = c_{\text{pol}} [S]^{0.5} [I]^{0.5}$  holds for PP, and the equation  $P_n = c_{\text{pol}} / [I]^{0.5}$  for DN and BP, where  $[S]$  is the emulsifier concentration in the aqueous phase,  $[I]$  is the initiator concentration in the aqueous phase, and  $[I]$  is the initiator concentration in the adsorptive layers of the emulsifier. At high initiator concentrations, a deviation from the above mentioned relationship was observed. The woman students N. Petukhova and I. Korobanova participated in the work. T. Krishan (Ref. 8: Candidate Dissertation, Moskovskiy Institut tekhnicheskoy khimicheskoy tekhnologii im. M. V. Lomonosova (Moscow Institute of Engineering Chemical Technology im. M. V. Lomonosov), 1969) is mentioned. There are 7 figures, 2 tables, and 12 references: 9 Soviet and 3 non-Soviet. The three references to English language publications read as follows: E. Wilson, J. Miller, E. Rowe, J. Phys. Chem. 53, 387, 1949; S. Maron, M. Eider, J. Ulevitch, J. Colloid Sci. 9, 89, 263, 374, 1954.

Card 3/04

Study of the emulsion (latec)...

S/ 90/61003,012-0081012  
B 24/B10

E. Gotsman. Trans. Inst. Rubber Ind. 26, 297, 4-2

ASSOCIATION: Moskovskiy Institut Khimicheskoy Tekhnologii (Moscow  
Institute of Fine Chemical Technology, F. Ye. Kozlovskiy  
Institute, L. Ya. Karpova Physicochemical Institute,  
Moscow, L. Ya. Karpova

SUBMITTED January 14, 1961

Fig. 1. Effect of the PP concentration on the stability of the  
aqueous phase. The curves are calculated according to the equation  
... according to the equation ...

Fig. 2. Effect of the PN concentration on the stability of the  
an emulsified ... according to the equation ...

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B103/B206

11.2211 also 2209.1372

AUTHORS: Spirin, Yu. L., Polyakov, D. K., Gantmakher, A. R., and  
Medvedev, S. S., Academician

TITLE: Polymerization of styrene, butadiene and isoprene, initiated  
by lithium ethyl in various media

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 139, no. 4, 1961, 899-902

TEXT: The authors investigated the separate polymerization and  
copolymerization of monomers: a) styrene, b) butadiene, and c) isoprene,  
which was initiated with lithium ethyl and carried out in 1) toluene, 2)  
triethylamine (amine), 3) diethyl ether, 4) dioxane, and 5) tetrahydro-  
furan (THF). Thus, the dependence of the reactivity of these monomers on  
their structure and on polymerization conditions was to be clarified.  
The methods were described in previous studies (Ref. 1: Yu. L. Spirin et  
al., Vysokomolekul. soyed., 2, 1082 (1960); Ref. 2: L. M. Lanovskaya et al.,  
ibid., 1391). In all three cases, the molecular weight of the polymers  
increased in 1)-5) with the intensity of polymerization. Its dependence  
on the concentration C of the components was close to the ratio M/C (Ref.

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Polymerization of styrene, butadiene ...

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3; M. Szwarc & al. J. Am. Chem. Soc., 78, 2656 (1956), Ref. 4; F. Welch, ibid. 81, 1345 (1959)). The walls of the dilatometer were subjected to special treatment when the investigation took place at a low concentration of the initiator ( $\sim 10^{-5}$  mole/l). In these cases the concentration of the active centers was determined on the basis of the molecular weight. In the presence of 2) to 5), a bulb dilatometer melted from one piece of quartz was used for polymerization, the concentration of active centers being determined spectrophotometrically at a given wavelength. 1): Even at relatively low concentrations of the initiator, deviations from the proportional dependence of the rate on the concentration of the initiator occurred. The rules observed were previously explained (Ref. 1) by the formation of mutually associated "live" polymers in hydrocarbon media. They are inactive during polymerization. The association of the active centers was also proved viscosimetrically: The viscosity of the solutions of the "live" Li polyisoprene in toluene dropped considerably due to deactivation. The equilibrium between the associates and the monomer centers which are active during polymerization, is displaced with the temperature rise in the direction of the latter. Thus, the activation energy of the process is lowered. This takes place even at a

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concentration of the initiator of  $\sim 0.5 \cdot 10^{-4}$  mole/l. Thus, an association exists also under these conditions. The authors established that the association of the active centers increases as follows: Li polystyrene < Li polyisoprene < Li polybutadiene. The relative reactivity of the monomers increases as follows: styrene < isoprene < butadiene. 2) - 5). Polymerization is accelerated with the introduction of these solvents, but the activation energies are reduced correspondingly. THF (0.6%) which reduces the activation energy of styrene polymerization in toluene from 14.5 to 6.8, has the strongest effect. However, the activation energy of isoprene polymerization in THF rises with temperature increase. This seems to be explained by a degenerate passing on of the chain through the monomer (Ref. 6: S. Ye. Bresler et al., ZhTF, ser. B, 28, 114 (1958)). The association of the "live" polymers is considerably reduced in the presence of 2) to 5), since 2) to 5) form complexes with lithium. Association of the Li polystyrene is absent in the medium of 2) to 5) (there is a proportional dependence between the rate of polymerization and the concentration of the initiator); Li polyisoprene is slightly associated in amine; Li polybutadiene is considerably associated in

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amine. Even in THF, which is a solvent of high dissolving capacity, some associations of Li polybutadiene occur. This the authors believe to be a dependence of the degree of association of the active centers on their construction. In previous studies (Ref.1; Ref. 7; Yu. L. Spirin & al., Vysokomolek. soyed., 1, 1258 (1959)) the authors explained the peculiarities of the polymerization of non-polar monomers of the above type by the participation of the lithium component, besides the carbanion component, in the growth of the chain. The introduction of 2) to 5) which form complexes with the lithium component of the catalyst, reduces the effect of this component on the growth of the chain. The mechanism of the process is changed correspondingly. It approaches a typical anionic polymerization in the presence of admixtures of high dissolving capacity (THF). The authors presume that the reduction of the activation energy with increasing THF concentration takes place due to the destruction of associates as well as through a change of the complexes between THF and the active centers, and through the increase of the dielectric constant of the medium. In spite of different dielectric constants of ether and dioxane (4.33 and 2.28 at 20°C), the polymerization of styrene in it proceeds at a comparable rate and activation energy. The authors also

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investigated the composition of copolymers in the systems styrene-isoprene and styrene-butadiene in the presence of 2) to 5), and calculated the copolymerization constants for amine and THF. The relative portion of styrene in the copolymer rises in these systems when 2) to 5) are introduced. It may be seen from the data that the effect of the solvents on separate polymerization and copolymerization is not always the same. In the presence of THF, the copolymers are strongly enriched with styrene and correspond to the compositions from typical anionic processes (D. E. Kelley, A. V. Tobolsky, J. Am. Chem. Soc., 81, 1597 (1959)). The relative reactivity of monomers increases in THF, e. g., isoprene < butadiene < styrene. The authors presume that the reactivity of monomers on separate polymerization in polar media is changed in the same sequence as in the case of copolymerization. The effect of solvents 1) to 5) on polymerization largely depends on their electron-donor capacity. Relatively weak electron donors like amine, ether, or dioxane change the polarization of the Li-C bond only slightly. In individual cases, they even increase the activation energy of chain growth as compared with hydrocarbon solvents. The strong electron donors (THF), however, entirely eliminate the effect of lithium. Thus, the polarization

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of the Li-C bond is abruptly increased. The process is here brought nearer to that of typical anionic polymerization, where the carbanion forms the active center. There are 1 figure, 2 tables, and 8 references: 4 Soviet-bloc and 4 non-Soviet-bloc. The most important references to English-language publications see in the body of the abstract.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova  
(Physicochemical Institute imeni L. Ya. Karpov)

SUBMITTED: April 24, 1961

Card 6/6

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28648  
S/020/61/139/006/013/022  
B103/B101

AUTHORS: Arest-Yakubovich, A. A., Gantmakher, A. R., and Medvedev, S. S.,  
Academician

TITLE: Anionic polymerization in the presence of aromatic compounds

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 139, no. 6, 1961, 1351-1353 X

TEXT: The aim of this article was to find out whether aromatic hydrocarbons participate in an anionic chain growth. The authors found that the anionic polymerization of styrene (in tetrahydrofuran, initiated by sodium-aromatic complexes) is strongly retarded by anthracene. The retardation depends on the ratio of anthracene to styrene. Anthracene exerts an inhibitory effect both if it is added together with the initiator (sodium naphthalene or sodium anthracene) and if a styrene - anthracene mixture is added to "live" polystyrene obtained from sodium naphthalene or sodium diphenyl. The authors conclude that this process takes place with a constant number of active centers. This number is equal to the amount of the initiator used and no chain transfer takes place. Hence, the mentioned retardation is not related to the decrease of the number of  
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Anionic polymerization in the presence ... B103/B101

active centers as a result of the shift of the initiation equilibrium of  $A^* + C \rightleftharpoons A + C^*$  (II) to the left-hand side. A is anthracene and C styrene; the asterisks denote the ion radicals, i. e. the molecules having an excess electron. Hence, the excess electrons completely pass from anthracene into styrene. The lacking of  $A^*$  in the system was also spectrophotometrically confirmed. The complete consumption of  $A^*$  is explained by an irreversible consumption of  $C^*$  as a result of the reaction with the monomer and of recombination. Also the low monomer consumption in the initial stage which results from an abrupt retardation of the growth reaction in the presence of anthracene contributes to this effect. This retardation is probably related to the participation of anthracene in growth processes. It is assumed that a joint polymerization of anthracene and styrene takes place since anthracene is very active in the radical reactions. Publications contain no data on the participation of anthracene in anionic copolymerization. The kinetic effects observed by the authors justify the assumption that anthracene adds to the carbanions of styrene thus forming a rather stable and little active anion since the charge is considerably delocalized. This assumption was confirmed

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Anionic polymerization in the presence ...

experimentally. An amount of anthracene that was three times higher than the number of active centers was added to a solution of "live" polystyrene (obtained with sodium naphthalene). The electron spectra showed that anthracene copolymerizes with styrene. In contrast to ordinary "live" polymer whose spectrum is essentially changed already one day after the production, the spectrum of the polymer produced from anthracene remains practically unchanged for three days. The shift of the maximum can be explained either by the complex formation between anthracene and the active centers of polymerization which takes place according to M. Levy (Ref. 7, see below) or the shifted maximum 445 m $\mu$  corresponds to the anthracene carbanions at the ends of the polymer chains. Large amounts of naphthalene (up to 50% as referred to styrene) influence neither the reaction rate nor the molecular weight. However, they essentially change the spectrum of the "live" polymer. The maximum at 340m $\mu$  disappears while maxima at 430 and 550 m $\mu$  reappear. The polymer is capable of absorbing further monomer portions while keeping its changed spectrum. The polymerization of a less active monomer as, e. g., butadiene, is more strongly inhibited by anthracene. Thus, anionic polymerization of butadiene at 20°C practically stops already at an anthracene-to-butadiene

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ratio of 1 : 30. It is concluded from the spectral data that "live" polybutadiene reacts with anthracene in the same way as "live" polystyrene. There are 2 figures and 11 references, 3 Soviet and 8 non-Soviet. The two most important references to English-language publications read as follows: Ref. 1: M. Szwarc, M. Levy, R. Milkovich, J. Am. Chem. Soc., 78, 2656 (1956); Ref. 7: M. Levy, F. Cohen-Basidan, Polymer, 1, 517 (1960).

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova  
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SUBMITTED: May 18, 1961

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29012

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B106/B110

AUTHORS: Zabolotskaya, Ye. V., Khodzhemirov, V. A., Gantmakher, A. R.,  
and Medvedev, S. S., Academician

TITLE: Polymerization and copolymerization of isoprene under the  
action of  $\alpha\text{-TiCl}_3 \cdot \text{Al}(\text{C}_2\text{H}_5)_3$

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 140, no. 4, 1961, 825 - 828

TEXT: The authors studied the kinetics of polymerization of isoprene alone and together with styrene under the action of titanium trichloride and triethyl aluminum. To prevent precipitation of the polymer, benzene was used as solvent. Polymerization was carried out dilatometrically. The components were dosed in analogy with data in Ref. 1 (Ye. V. Zabolotskaya, A. R. Gantmakher, S. S. Medvedev, Vysokomolek. soyed., 2, No. 8, 1213 (1960)). All kinetic data were determined at  $75^\circ\text{C}$ , the degree of conversion did not exceed 10% by weight. Viscosity, molecular weights, and compositions of polymers were determined in dry argon atmosphere. The average-weight molecular weights ( $M_w$ ) were measured by the light scattering method, the average-number molecular weights ( $M_n$ ) by the osmotic method.

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Polymerization and copolymerization...

The compositions of copolymers were determined by IR spectroscopy. The authors thank N. V. Makletsova and A. P. Golovina for measuring the molecular weights, and N. V. Desyatova for carrying out the spectrometric measurements. When studying the polymerization of isoprene, polymerization rate and titanium chloride concentration per unit volume were found to be linearly dependent. This indicates that the number of active centers is determined by the concentration of the  $\text{TiCl}_3 \cdot \text{Al}(\text{C}_2\text{H}_5)_3$  complex on the surface of  $\text{TiCl}_3$ . All experiments were performed with  $\text{TiCl}_3$  of a medium grain size of  $1.5\text{-}2\mu$ . The relation between polymerization rate and monomer concentration, however, is not linear, polymerization rate increases more slowly than isoprene concentration. Polymerization probably takes place on the catalyst surface via complex formation of the monomer with the titanium component of the catalyst, and subsequent penetration of a polarized monomer into the Al-C bond. The total activation energy of polymerization was determined to be 13 kcal/mole from the temperature dependence of the polymerization rate of isoprene at  $60\text{ - }95^\circ\text{C}$ . Table 1 shows the results of molecular weight determinations. The ratio  $M_w/M_n$  is close to unity, which indicates that the resultant

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polyisoprene exists in the monodisperse phase. The molecular weight depends slightly on the monomer concentrations. When studying the copolymerization of isoprene and styrene, the composition of copolymers and the polymerization rate were determined as a function of the composition of the initial mixture (Figs. 2, 3). It may be seen from Fig. 2 that the copolymers are considerably enriched in isoprene as compared with the composition of the initial mixture. Fig. 3 shows that the rate of copolymerization is much lower than the rates of separate polymerizations of isoprene and styrene. The inhibitory effect of isoprene is particularly high if it is added to styrene in small quantity. The inhibitory effect is due to the reduced reaction rate when a polarized monomer enters the Al-C bond of the transition complex of the chain with the catalyst. This decrease in rate takes place when the styrene molecule in the end group of the chain is replaced by isoprene. It was found that the molecular weights of polymers vary cymbately with a change in polymerization rate at different compositions of the initial mixture (comparison of data from Table 1 with Fig. 3). There are 3 figures, 1 table, and 8 references: 3 Soviet and 5 non-Soviet. The three references to English-language publications read as follows: J. Still, Chem. Rev., 58, 541

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Polymerization and copolymerization ...

(1958); G. Natta, J. Pasquon, Advances in Catalysis, 11, 68 (1959); N. G. Gaylord, Trans. N. Y. Acad. Sci., 22, No 6, 387 (1960).

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: May 29, 1961

Table 1. Molecular weights of polymers (the molecular weight of polystyrene is of the order of  $10^6$  (Ref. 1)).  
Legend: (1) moles/liter; (2) moles/liter·min; (3) isoprene in the initial mixture, mole%; (4) molecular weight· $10^{-3}$ .

[C <sub>6</sub> H <sub>5</sub> ] мол/л ①	[C <sub>6</sub> H <sub>5</sub> ] мол/л ①	[Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ] ·10 <sup>3</sup> , мол/л ①	TiCl <sub>4</sub> ·10 <sup>3</sup> мол/л ①	V·10 <sup>3</sup> мол л·мин ②	Изопрен в исходн. смеси, мол.% ③	[η]	Мол. вес·10 <sup>-4</sup> ④	
							M <sub>w</sub>	M <sub>n</sub>
0.97	—	3.62	3.63	—	100	2.15	600	600
3.03	—	3.72	3.82	—	100	2.25	700	690
7.35	0.68	3.84	3.17	11.8	67.3	2.30	—	600
10.85	1.01	3.58	3.22	5.2	48.5	2.00	—	375
10.41	3.60	4.26	5.86	—	13.0	2.00	—	385

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S/190/62/004/005/011/026  
B110/B144

5 2200  
AUTHORS: Solovykh, D. A., Arest-Yakubovich, A. A., Cantmakher, A. R.,  
Medvedev, S. S.

TITLE: Polymerization of styrene and butadiene initiated by sodium  
naphthalene in weakly polar media

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 5, 1962,  
702-703

TEXT: The activation energy and rate constants of the homogeneous polymerization of styrene and butadiene with organosodium initiators in hydrocarbon media in the presence of small tetrahydrofuran additions were determined for the first time by a two-stage method. First, "live" polymers were obtained by preliminary polymerization of  $\sim 1/6$  of the monomer with sodium naphthalene in a tetrahydrofuran medium, and were then used as polymerization initiators in toluene or cumene with tetrahydrofuran. The polymerization rate was measured between  $-60$  and  $-35^{\circ}\text{C}$  and the initiator concentration was determined from  $c = 2m/M$ , where  $m$  is the amount of polymerized monomer in g,  $c$  is the number of initiator moles, and  $M$  is the

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molecular weight of the polymer. Toluene caused chain transfer during butadiene polymerization with 6.5% tetrahydrofuran. The polymerization rate of styrene and butadiene in toluene was found to increase with transition from organolithium to organosodium initiators. There is 1 table.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova  
(Physicochemical Institute imeni L. Ya. Karpov)

SUBMITTED: March 31, 1961

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Polymerization of styrene and ...

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(2) Содержа- ние ТГФ, об. %	(3) Мономер	(4) Исходная концен- трация мо- номера, моль/л	(5) Раствори- тель	(6) Концент- рация НН, моль/л	(7) Темпера- тура поли- мериза- ции, °C	(8) E, ккал/моль	(9) k-50°, л/моль·с
2	Стирол (10)	1,1	Толуол (12)	0,002	-60 - -45	8000	0,15
2,5	" "	1,14	Кумол (13)	0,002	-60 - -45	7700	0,14
11,5	" "	0,84	Толуол (12)	0,004	-50	—	—
3,5	Бутадиен (11)	1,3	" "	0,003	-50 - -40	—	0,008
6,5	" "	2,5	Кумол (13)	0,002	-50 - -35	7500	0,006

Table. Polymerization of styrene and butadiene in the presence of sodium naphthalene in hydrocarbon solvents with tetrahydrofuran additions. Legend: (2) Tetrahydrofuran content, % by volume; (3) monomer; (4) initial monomer concentration, moles/liter; (5) solvent; (6) sodium naphthalene concentration, moles/liter; (7) polymerization temperature, °C; (8) E, kcal/mole; (9) k<sub>-50°C</sub>, liter/mole·sec; (10) styrene; (11) butadiene; (12) toluene; (13) cumene.

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S/076/62/036/011/016/021  
B101/B180

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AUTHORS: Bass, S. I., and Medvedev, S. S.

TITLE: The mechanism of the inhibiting action of phosphites in the oxidation of paraffinous hydrocarbons

PERIODICAL: Zhurnal fizicheskoy khimii, v. 36, no. 11, 1962, 2537-2539

TEXT: Triphenyl phosphite (I) and tri-n-butyl phosphite (II) were studied, with the oxidation of hexadecane at 140-160°C and atmospheric pressure. The peroxides content of the reaction mixture was determined iodometrically, and the consumption of I via the quantitative reaction of I with tert-butyl hydroperoxide. A linear increase in the induction period and a decrease in the peroxide content were found with increasing concentration of I, as well as direct proportionality between the amount of oxygen absorbed and the initial concentration of I. When 4% I was added, no further peroxides were formed. The rate constants of the consumption of I ( $k \cdot 10^7$  moles/liter·sec) were 66.5 at 160°C, 39.2 at 150°C, and 23.3 at 140°C, the activation energy was 21 kcal/mole. II proved much less active than I. Addition of 1.2% phenol had no effect on the induction

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The mechanism of the inhibiting...

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period, but lowered the oxidation rate and oxygen consumption. From the

reactions  $RH + O_2 \xrightarrow{k_0} \dot{R} + HO_2\cdot$ ;  $\dot{R} + O_2 \xrightarrow{k_1} RO_2\cdot$ ;  $RO_2\cdot + RH \xrightarrow{k_2} ROOH + \dot{R}$ ;

$RO_2\cdot + P \xrightarrow{k_3} \dot{R}O + P=O$ ;  $\dot{R}O + P \xrightarrow{k_4} \dot{R} + P=O$ ;  $ROOH + P \xrightarrow{k_5} ROH + P=O$ , where

P is the phosphite, P=O the corresponding phosphate, and assuming that  $k_2 \ll k_3$ , the induction period was found to be  $\tau = P_0/2w_0$ , where  $P_0$  is the initial phosphite concentration, and  $w_0$  is the initiation rate. Hence, this assumption leads to a linear function corresponding to the function  $\tau = f(P_0)$  which had been found experimentally. The more intensive action of I, as compared with II, is attributed to the effect of the electron acceptor phenyl groups. The inhibiting effect observed after the induction period is based on a competing reaction of the phenol formed by hydrolysis of I, and explains the result of the direct addition of phenol. There are 3 figures. y

ASSOCIATION: Moskovskiy institut tonkoy khimicheskoy tekhnologii im.  
M. V. Lomonosova (Moscow Institute of Fine Chemical  
Technology imeni M. V. Lomonosov)

Card 2/3

The mechanism of the innibiting...

S/076/62/036/011/016/021  
B101/B180

SUBMITTED: April 4, 1962

Card 3/3

15.8610.

40567  
S/020/62/146/002/009/013  
B101/B144

AUTHORS: Spirin, Yu. L., Gantmakher, A. R., Medvedev, S. S.  
Academician

TITLE: Association of organolithium compounds and its role during  
polymerization

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 146, no. 2, 1962, 366-371

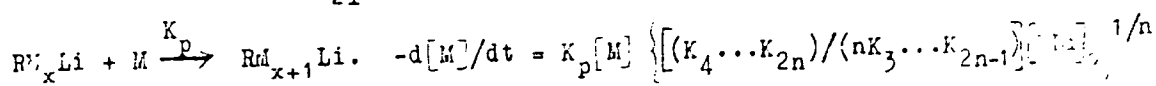
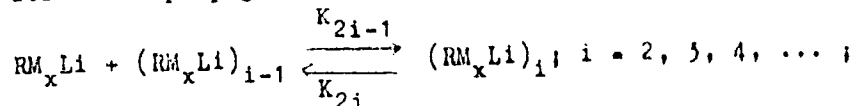
TEXT: When polymerization is initiated by organolithium compounds, the polymerization rate increases more slowly than the concentration of the initiator, owing to deactivation of the active centers by association. The authors studied the effect of the polymer carbanion structure on the association degree during the polymerization of styrene, isopropene, or butadiene initiated by ethyl lithium. The shift of the absorption band toward greater wave lengths and the change in optical density of the band were observed in order to study the conversion of ethyl lithium into associates with the polymer carbanion. The specific effect of the polymers was found to be an increase in initiation rate following the sequence isoprene < butadiene < styrene. An examination of the equation

Card 1/3

S/020/62/146/002/003/013  
B101/B144

Association of organolithium ...

$-d[M]/dt = K[M][LiR]^{1/n}$  (1),  $n > 1$  for chain propagation showed that  $n$  depends on the carbanion structure. For polystyrene  $n \approx 2$ , for polyisoprene  $n \approx 3 - 4$ , and for polybutadiene  $n \approx 5 - 6$ . The following reaction for chain propagation is established:



which shows good agreement with the experimental equation (1). The slight change in activation energy brought about by changing the initiator concentration approximately the  $10^3$ -fold, proves the stability of the associates and the constancy of their composition. The active centers were mainly in an associated state even at an ethyl lithium concentration of  $10^{-5}$  moles/l. There are 3 figures and 1 table. The most important English-language references are: F. Welch, J. Am. Chem. Soc., 81, 1345 (1959); D. I. Worsfold, S. Bywater, Canad. J. Chem. 38, 1891, (1960).

Card 2/3

Association of organolithium ...

S/020/62/146/002/009/013  
B101/B144

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: May 31, 1962

Card 3/3

MEDVEDEV, S.S., GANTMAKHER, A.R.

Concerning the directed growth of chains in the process of anionic-coordination polymerization.

Report submitted for the International Symposium of Macromolecular chemistry  
Paris, 1-6 July 63

KOLESNIKOV, G.S., otv. red.; ANDRIANOV, K.A., red.; DOGADKIN, B.A., red.; DOLGOPLOSK, B.A., red.; YENIKOLOPYAN, N.S., red.; KARGIN, V.A., red.; KOZLOV, P.V., red.; KOROTKOV, A.A., red.; KORSHAK, V.V., red.; LAZURKIN, Yu.S., red.; MEDVEDEV, S.S., red.; MIKHAYLOV, N.V., red.; PASYNSKIY, A.G., red.; SLONIMSKIY, G.L., red.; SMIRNOV, V.S., red.; TSVETKOV, V.N., red.; FREYMAN-KRUPENSKIY, K.A., tekhn. red.

[Carbochain high-molecular weight compounds] Karbotsepnnye vysokomolekuliarnye soedineniia; sbornik statei. Moskva, Izd-vo AN SSSR, 1963. 287 p. (MIRA 17:1)

S/190/63/005/004/009/020  
B101/B220

AUTHORS: Krishan, T., Margaritova, M. F., Medvedev, S. S.

TITLE: Regularities of emulsion polymerization. I. Polymerization of methyl methacrylate

PERIODICAL: Vysokomolekulyarnyye soedineniya, v. 5, no. 4, 1963, 535-541

TEXT: The study refers to the polymerization of methyl methacrylate at 40 - 55°C, emulsified with MK(MK) emulsifier (sodium salt of the sulfonic acids of paraffin hydrocarbons) or sodium laurate, initiated with benzoyl peroxide or potassium persulfate. Results: (1) In the presence of MK and benzoyl peroxide the polymerization rate  $w$  is proportional to the concentration of the emulsifier up to  $c_{em} \leq 4$  g/100 ml. With higher  $c_{em}$ ,  $w$  depends no longer on  $c_{em}$ . (2) In the presence of sodium laurate and benzoyl peroxide  $w = kc_{em}$ . (3) With MK and potassium persulfate  $w = kc_{em}^{0.5}$ . With  $c_{em} > 2$  g/100 ml,  $w$  becomes almost constant. (4) The reaction rate  $w$  is proportional to the square root of the initiator concentration  $c_{in}$ ; with  $c_{in} > 0.1$  g/100 ml,  $w$  becomes independent of  $c_{in}$  owing to termination.

Card 1/2



Regularities of emulsion ...

S/190/63/005/004/009/020  
B101/B220

ation processes. (5) Thus,  $w = k c_{em}^{0.5} c_{in}^{0.5}$  for MK;  $w = k c_{em}^{0.5} c_{in}^{0.5}$  for sodium laurate. (6) According to E. Willson et al. (J. Phys. Colloid Chem., 53, 357, 1949) and S. Maron et al. (J. Colloid Sci., 9, 89, 104, 347, 1954) the average number and surface of the polymer particles were determined at 50°C,  $c_{em} = 2 - 7.5$  g/100 ml;  $c_{in} = 0.0125 - 0.025$  g/100 ml and it was found that: (a) with given  $c_{em}$  and  $c_{in}$  the total surface is independent of the degree of polymerization and the ratio water-to-organic phase; (b) with increasing  $c_{em}$  the diameter of the polymer particles decreases and their number increases. Conclusion: Polymerization takes place in the surface layer of the emulsifier adsorbed on the surface of the polymer particles. There are 6 figures and 2 tables.

ASSOCIATION: Moskovskiy institut tonkoy khimicheskoy tekhnologii im. M. V. Lomonosova (Moscow Institute of Fine Chemical Technology imeni M. V. Lomonosov)

SUBMITTED: September 22, 1961

Card 2/2

YEVSTRATOVA, S.D.; MARGARITOVA, M.F.; MEDVEDEV, S.S.

Emulsion polymerization of vinyl compounds in the presence  
of organic acids and amines. Vysokom. soed. 5 no.10:1574-  
1579 0 '63. (MIRA 17:1)

1. Moskovskiy institut tonkoy khimicheskoy tekhnologii imeni  
Lomonosova.

L 16985-63

EPR/EWP(j)/EPF(c)/EWP(g)/EWT(m)/BDS AFFTC/ASD Ps-4/Pc-4/  
S/020/63/149/005/009/018

Pr-4 RM/WW/JD

AUTHOR: Basova, R. V., Arest-Yakubovich, A. A., Solovykh, D. A.,  
Desyatova, N. V., Gantmakher, A. R., and Medvedev, S. S. 79

TITLE: Polymerization of butadiene in the presence of alkali metals  
and their compounds in different media 27

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 149, no. 5, 1963, 1067-1070

TEXT: Literature on the polymerization of dienes, initiated by alkali metals and their compounds, notes that the proportion of structures characteristic of the anion type of polymerization, contrary to expectations, decreases with increasing polarity of the Me-R bond (Me -- alkali metal) in hydrocarbon media. The authors of this work, devoted to investigation of the effect of polymerization conditions on the structure of butadiene, pay special attention to this problem. The investigation was performed under vacuum conditions, with prior thorough cleaning of monomers and solvents. The results obtained show that the increase in the proportion of 1,2-structures of polybutadiene and 3,4-structures of polyisoprene, observed upon transition from potassium to sodium compounds in a hydrocarbon medium is due to the presence of impurities solvating the opposite-charged ions. There are 2 tables.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov) SUBMITTED: January 10, 1963

Card 34

ACCESSION NR: AP4019980

8/0020/64/154/006/1402/1405

AUTHOR: Teleshov, E. N.; Teleshova, A. S.; Dasyatova, N. V.; Pravednikov, A. N.;  
Medvedev, S. S. (Academician)

TITLE: Gas release and formation of double bonds during radiolysis of  
polyisobutylene (PIB)

SOURCE: AN SSSR. Doklady\*, v. 154, no. 6, 1964, 1402-1405

TOPIC TAGS: gas, double bond, radiolysis, polyisobutylene, Co sup 60, linear  
electron accelerator, free radical

ABSTRACT: Industrial polyisobutylene films, prepared by evaporation of weak  
solutions of a polymer in carbon tetrachloride were used. Co<sup>60</sup> (about 20 000 gm-  
equivalent Ra) and a linear electron accelerator (200 kev) were the source of  
ionizing radiation. Before irradiation, the films were evacuated to about 10<sup>-5</sup> mm  
Hg during heating to 70C for 24 hours. The degree of destruction was estimated  
from viscosimetric data. The results indicate that the loss of free radicals in  
PIB at a temperature above the vitrification temperature is not accompanied by  
either a formation of gaseous products or the development of double bonds in the

Card 1/2

ACCESSION NR: AF4019980

polymer. Orig. art. has: 4 figs., 2 tables.

ASSOCIATION: none

SUBMITTED: 24Oct63

DATE ACQ: 23Mar64

ENCL: 00

SUB CODE: CH

NO REF SOV: 003

OTHER: 005

Card 2/2

LYUDVIG, Ye.B. GANTMAKHER, A.R.; MEDVEDEV, S.S., akademik

Mechanism of cationic polymerization in the presence of metal  
halides. Dokl. AN SSSR 156 no. 5:1163-1166 Je '64.  
(MIRA 17:6)

1. Fiziko-khimicheskiy ins'titut im. L.Ya.Karpova.

ACCESSION NR: AP4030788

S/0020/64/155/004/0890/0892

AUTHOR: Diakonesku, I.; Medvedev, S. S. (Academician)

TITLE: Some peculiarities of polymerizing butadiene in the presence of complex cobalt catalysts.

SOURCE: AN SSSR. Doklady\*, v. 155, no. 4, 1964, 890-892

TOPIC TAGS: butadiene, polymerization, complex cobalt catalyst, diisobutylaluminum chloride, polymerization rate, polymer molecular weight, microstructure, catalyst concentration, catalyst component ratio, chain termination, polybutadiene

ABSTRACT: The polymerization of butadiene in benzene solution in the presence of catalyst systems consisting of an alcohol complex of cobalt chloride ( $\text{CoCl}_2 \cdot x\text{C}_2\text{H}_5\text{OH}$ ) and of diisobutylaluminum chloride ( $\text{AlR}_2\text{Cl}$ ) was studied to determine the relationship between the rate of polymerization, molecular weight, and microstructure of the polymer and the concentration of the catalysts and their ratio. It was found that water has a strong influence on polymerization rate and molecular weight. In the absence of water only a small amount of very low molecular

Card 1/2

ACCESSION NR: AP4030788

weight polymer is formed. With increasing amounts of water the molecular weight increases since water limits the chain termination reaction. However, the water also reacts with the components of the catalyst system, decreasing the effective concentration of the catalyst, and thus decreasing polymerization rate. The polymerization rate increases initially proportionally to the increase in  $\text{CoCl}_2 \cdot x\text{C}_2\text{H}_5\text{OH}$  concentration, then reaches a limit. The limit is lower with a smaller initial  $\text{H}_2\text{O}$  concentration. The polybutadiene molecular weight increases as the concentration of either of the catalyst components decreases. The data is insufficient to prove the nature of the complex cobalt polymerization process. It is concluded, however, that it is impossible to determine the true mechanism of this type of process without considering the significant role that water plays. Orig. art. has: 3 figures.

ASSOCIATION: Moskovskiy institut tonkoy khimicheskoy tekhnologii im. M. V. Lomonosova (Moscow Institute of Fine Chemical Technology)

SUBMITTED: 02Jan64

DATE ACQ: 30Apr64

ENCL: 00

SUB CODE: 00

NO REF SOV: 005

OTHER: 003

Card 2/2



KARDASH, I.Ye.; PRAVEDNIKOV, A.N.; MEDVEDEV, S.S., akademik

Thermal degradation of polyethylene terephthalate. Dokl.  
AN SSSR 156 no. 3:658-661 '64. (MIRA 17:5)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova.

ACCESSION NR: AP4023496

S/0069/64/026/002/0168/0173

AUTHOR: Gritskova, I. A.; Medvedev, S. S.; Margaritova, M. F.

TITLE: Polymerization of styrene in the presence of non-ionic emulsifiers. 1.  
Polymerization of styrene in the presence of the emulsifier OS-20

SOURCE: Kolloidnyy zhurnal, v. 26, no. 2, 1964, 168-173

TOPIC TAGS: styrene polymerization, polymerization initiator, azobisisobutyronitrile, emulsifier influence, ethyleneoxide hydrocarbon mixture, polymerization rate, polymerization rate dependency, ionic emulsifier, anionic emulsifier, latex particle, polymer chain formation, hydrocarbon phase, aqueous phase, none ionic emulsifier

ABSTRACT: This emulsifier is the reaction product of 20 moles of ethylene oxide with a mixture of higher fatty acid alcohols of the general formula  $R - O(CH_2-CH_2O)_nH$  where R is the alkyl groups containing 16-18 carbon atoms, n an average of 20. The preparation of styrene, the initiator azobisisobutyronitrile, experimental equipment and procedures are described. The polymerization rate was determined with a dilatometer. The results are figured and tabulated for various

Card 1/3

ACCESSION NR: AP4023496

emulsifier concentrations in the aqueous phase and for the polymerization rates. The process, which proceeded essentially at a constant rate after initial growth up to 2.3 g/100 ml emulsifier concentration, differs considerably from that observed with ionic emulsifiers. This difference consists mainly in the average diameter of the latex particles which is larger by one order of magnitude and does not depend upon the polymerization degree nor the concentration of the emulsifier. The average molecular weight of the forming polystyrene increased with an increase in the degree of polymerization degree, in contrast to reactions with ionic emulsifiers, indicating possible intraparticle polymerization. The polymerization rate depended upon the initiator concentration only at concentrations of up to 0.225 g/1000 milliliters of the aqueous phase; this limit is higher with ionic emulsifiers. Initiation proceeded with participation of the emulsifier in the surface layers of the latex particles. The number of stable latex particles, thus also the rate of polymerization, were shown to depend upon the ratio monomer/emulsifier (aqueous) phase, which dependency is also absent with ionic emulsifiers. The overall activation energy of polymerization was 19.8 kcal/mole. The theoretical results agreed satisfactorily with experimental data. Orig. art. has: 4 figures and 5 formulas.

Card 2/3

ACCESSION NR: AP4023496

ASSOCIATION: Moskovskiy institut tonkoy khimicheskoy tekhnologii im. M. V.  
Lomonosova (Moscow Institute of Technology of Fine Chemicals)

SUBMITTED: 05Jul63

DATE ACQ: 15Apr64

ENCL: 00

SUB CODE: GC, OC

NO REF SOV: 002

OTHER: 002

Card 3/3

S/190/63/005/004/010/020  
B101/B220

**AUTHORS:** Krishan, T., Margaritova, M. F., Medvedev, S. S.

**TITLE:** Regularities of emulsion polymerization. II. Polymerization of chloroprene and vinylidene chloride

**PERIODICAL:** Vysokomolekulyarnyye soyedineniya, v. 5, no. 4, 1963, 542-546

**TEXT:** The study refers to the polymerization of chloroprene and vinylidene chloride, emulsified with MK (MK) emulsifier (sodium salt of sulfonic acids of paraffin hydrocarbons) or sodium laurate, after initiation with benzoyl peroxide, potassium persulfate, hydrogen peroxide, sodium perborate or azoisobutyric dinitrile. The polymerization rate  $w$  (g polymer per 100 ml·hr) was determined. Data found for chloroprene: (1) In the presence of MK and potassium persulfate  $w = k_p c_{em}^{0.5} c_{in}$ , where  $c_{em}$  is the concentration of the emulsifier and  $c_{in}$  the concentration of the initiator; (2) In the presence of benzoyl peroxide, however,  $w$  passes through a maximum with  $c_{in} \sim 0.05$  g/100 ml of the aqueous phase whatever the emulsifier used. For vinylidene chloride it was found that, using water-Gard 1/2

Regularities of emulsion ...

8/190/63/005/004/010/020  
B101/B220

soluble initiators,  $w = k_0 c_{em}^n$  where  $0.5 > n > 0.25$ , and using oil-soluble initiators (benzoyl peroxide and azoisobutyric dinitrile)  $w = k_0 c_{em}^{0.5}$ . This different behavior of vinylidene chloride is caused by weaker adhesion of the emulsifier to the polymer particles. There are 5 figures.

ASSOCIATION: Moskovskiy institut tonkoy khimicheskoy tekhnologii im. M. V. Lomonosova (Moscow Institute of Fine Chemical Technology imeni M. V. Lomonosov)

SUBMITTED: September 22, 1961

Card 2/2

POLYAKOV, D.K.; SPIRIN, Yu.L.; GANTMAKHER, A.R.; MEDVEDEV, S.S., akademik

Nature of carbon - alkali metal bond studied by means of electron  
absorption spectra. Dokl. AN SSSR 150 no.5:1051-1054 Je '63.  
(MIRA 16:8)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova.  
(Chemical bonds) (Carbanions---Absorption spectra)

L 18897-63 EPR/EFF(c)/EWP(j)/EWT(m)/BDS ASD Ps-l/Pr-l/Pc-l RM/WW/  
 ACCESSION NR: AP3006596 S/0020/63/151/006/1347/1349 MAY/JFW

AUTHORS: Pravednikov, A. N.; Kardash, I. Ye.; Bazov, V. P.; Yeliseyeva, N. V.;  
Sharpaty\*y, V. A.; Medvedev, S. S. (Academician)

TITLE: Free-radical polymerization of triazine cycles 77

SOURCE: AN SSSR. Doklady\*, v. 151, no. 6, 1963, 1347-1349

TOPIC TAGS: free radical, polymerization, triazine, triazine cycle, free-radical polymerization

ABSTRACT: The present article reports the results of spectroscopic and electron paramagnetic resonance analysis of the polymers obtained by heating triazines with perfluoracetone as a source of  $CF_3$  radicals at 520°C. The free-radical polymerization of triazine cycles, evidently representing addition of the free radical to the cycle on the double bond with subsequent opening of the cycle, must be accompanied at high temperatures by depolymerization, by a splitting of the monomeric by a unit from the polymeric radical. Orig. art. has: 1 formula 2 figures.

ASSOCIATION: none

SUBMITTED: 28May63

SUB CODE: CH

Card 1/1

DATE ACQ: 27Sep63

NO REF SOV: 000

ENCL: 00

OTHER: 000



KOZLOV, P.V., otv. red.; ANDRIANOV, K.A., red.; DOGADKIN, B.A., red.;  
DOLGOPLOSK, V.A., red.; YENIKOLOPYAN, N.S., red.; KARGIN,  
V.A., red.; KOLESNIKOV, G.S., red.; KOROTKOV, A.A., red.;  
KORSHAK, V.V., red.; LAZURKIN, Yu.S., red.; MEDVEDEV, S.S.,  
red.; MIKHAYLOV, N.V., red.; PASYNSKIY, A.G., red.;  
SLONIMSKIY, G.L., red.; SMIRNOV, V.S., red.; TSVETKOV, V.N.,  
red.; FREYMAN-KRUPENSKIY, D.A., tekhn. red.

[Adhesion of polymers] Adgeziia polimerov; sbornik statei.  
Moskva, Izd-vo AN SSSR, 1963. 142 p. (MIRA 16:10)  
(Polymers) (Adhesion)



L 15706-65 EWC(j) EWT(m)/EPT(c)/EPT(n)-2/EWP(j)/T/EWA(h)/EWA(l) Pc-L/Pr-L/Pu-L/  
 Feb AFFTC/ASD-3/SSD/RPL/ESD(t)/ESD(gs)/RAEM(c)/ESD(t)/RAEM(l)/SSD/BSO/AFWL/ASD(a)-5/  
 ACCESSION NR: AP044277 AS(mp)-2 CG/RM/E/0192/64/005/004/0627/0629

WW/JFW

AUTHORS: Teleshov, E.N.; Sharpaty, V.A.; Pravednikov, A.N.

Medvedev, S. S.

TITLE: Some changes in EPR spectra of irradiated polyisobutylene

SOURCE: Zhurnal strukturnoy khimii, v. 5, no. 4, 1964, 627-629

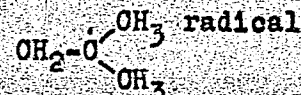
TOPIC TAGS: polyisobutylene, electron paramagnetic resonance electron, irradiation, uv. radiolysis, free radical, free radical recombination, polymer radiolysis

ABSTRACT: The irradiation of polyisobutylene (PIB) at liquid nitrogen temperature leads to accumulation of free radicals in it. The EPR spectrum of these radicals is a doublet with approximately 22 oersted splitting which is attributed to  $-O(CH_2)_2-\dot{O}H$  radical (I). In this work an attempt is made to obtain by the EPR method some additional information on the nature and properties of radical products which are formed during radiolysis of PIB. It was found that heating of PIB samples, irradiated with  $\sim 10^{22}$  ev/g dose of 1.6 mev electrons at -180°C leads, along with the destruction of primary radicals, to irreversible changes in EPR spectrum. In it the doublet is converted to a spectrum which consists of seven basic lines with addition of

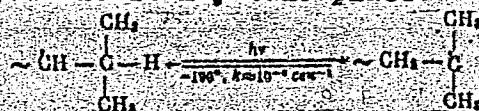
Card 1/3

L 15706-65  
ACCESSION NR: APA044277

fine structure. This spectrum may be ascribed to



which is produced as a result of addition of isobutylene molecule to radical (I). Isobutylene is produced during radiolysis of PIB. During low temperature radiolysis of PIB radical (II) is not detectable by the EPR method because radicals which are formed during breakage of the radical chain immediately enter recombination and disproportionation reactions. Irradiation of PIB at -600 (above vitrification temperature of the polymer) with simultaneous registration of EPR spectra enables one to find radicals (I) as well as radicals (II). PIB irradiated with UV at -600 for 5 min produces EPR spectrum similar to that of a mixture of PIB and isobutylene irradiated with electrons. It is suggested that under the influence of UV, isomerisation of primary radicals may take place:



Orig. art. has: 3 figures

Card 2/3

L 15706-65

ACCESSION NR: AP4044277

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova  
(Institute of Physical Chemistry)

SUBMITTED: 28Dec63

ENCL: 00

SUB CODE: OP, NP

NR REF SOV: C04

OTHER: 006

Card 3/3

ACCESSION NR: AP4009149

S/0190/64/006/001/0076/0080

AUTHORS: Zabolotskaya, Ye. V.; Khodzhandrov, V. A.; Gantmakher, A. R.; Medvedev, S. S.

TITLE: Polymerization and copolymerization of isoprene in the presence of alpha-TiCl<sub>3</sub> - Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>

SOURCE: Vyssokomolekulyarnyye soyedineniya, v. 6, no. 1, 1964, 76-80

TOPIC TAGS: polymerization, copolymerization, isoprene, styrene, catalyst, alpha titanium trichloride, triethyl aluminum, polymerization rate, copolymerization rate, activation energy

ABSTRACT: The polymerization of isoprene and its copolymerization with styrene were conducted in benzene, in the presence of alpha-TiCl<sub>3</sub> - Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>. The work was done at 75C, and the extent of polymerization did not exceed 10%. The polymers were reprecipitated by methanol and subjected to chemical analysis, determination of viscosity, molecular weight, and infrared spectroscopy. When 0.97-3.03 Mol/liter concentrations of isoprene (constant amount of catalyst) were tested, it was observed that the molecular weights of the obtained polymers were independent of the

1/2

Cord

ACCESSION NR: AP4009149

isoprene concentration, and that the increase in polymerization rate was not proportional to the concentration of the monomer. But the polymerization rate of isoprene proved to be proportional to the amount of  $TiCl_3$ , as is also the case with styrene and the olefines. Within a temperature range of 60-95C the yield of the polymer increased with the temperature. The overall activation energy of isoprene polymerization was estimated as  $13 \pm 0.5$  Kcal/Mole. The copolymerization of isoprene with styrene showed that an 8.5% addition of isoprene had a three- to four-fold lowering effect on the polymerization rate of styrene and on its molecular weight. The copolymers were greatly enriched in isoprene. The addition of styrene to the isoprene monomer lowered the polymerization rate of isoprene more moderately. Thanks are given to N. V. Makletsov and L. P. Golovin for molecular weight determinations, and to N. V. Desyatov for analysis of composition of the polymers. Orig. art. has: 2 tables and 8 charts.

ASSOCIATION: Fiziko-khimicheskii institut im. L. Ya. Karpova (Physical-Chemical Institute)

SUBMITTED: 07Aug62

DATE ACQ: 10Feb64

ENCL: 00

SUB CODE: CH

NO. REF SOV: 002

OTHER: 001

2/2

Card

ACCESSION NR: AP4009150

S/0190/64/006/001/0031/0085

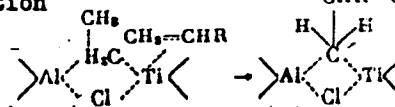
AUTHORS: Zabolotskaya, Ye. V.; Khodzhemirov, V. A.; Gantmakher, A. R.; Medvedev, S. S.

TITLE: Investigation of polymerization mechanism in isoprene with styrene catalyzed by  $\alpha$  -  $\text{TiCl}_3$  -  $\text{Al}(\text{C}_2\text{H}_5)_3$

SOURCE: Vy\*sokomolekulyarny\*ye soyedineniya, v. 6, no. 1, 1964, 81-85

TOPIC TAGS: polymerization, styrene, catalyst, isoprene, copolymer chain, monomer, differential composition

ABSTRACT: The mechanism of the  $\alpha$  -  $\text{TiCl}_3$  -  $\text{Al}(\text{C}_2\text{H}_5)_3$  combination catalyzed polymerization and copolymerization of isoprene and styrene has been investigated. It is assumed that in the primary initiation, the reaction



has no effect on the polymerization rate, and the polymer molecule dimension is limited by the reaction break-off of molecular chains. The polymerization rates for

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ACCESSION NR: AP4009150

styrene and isoprene then yield respectively  $V_A = k_A \cdot A \cdot \sigma_A$  The rate constant  $k_{BB}$

$$V_B = k_B \cdot B \cdot \sigma_B$$

of isoprene molecule transition is determined from the catalytic complex to the copolymer chain as  $4.15 \times 10^{-2} \text{ min}^{-1}$ . From differential rate equations describing the entry of each monomer (styrene A, isoprene B) into a copolymer, equations of differential composition of the polymer for each monomer are derived

$$\frac{dA}{dB} = \frac{[A] \frac{k_{A \cdot A} \cdot k_A [A]}{k_{A \cdot B} \cdot k_B [B]} + 1}{\frac{k_{B \cdot B} k_B}{k_{B \cdot A} k_A} + \frac{[A]}{[B]}}$$

, from which copolymerization constants  $r_A$  and  $r_B$  are

determined as being 0.1 and 6.0, respectively. It has been shown that inhibition of styrene polymerization by small isoprene additions is due to a decrease in styrene molecule addition rate to the end of the polymer chain when this unit is an isoprene rather than a styrene residue. Orig. art. has: 16 formulas, 1 figure, and 1 table.

ASSOCIATION: Fiziko-khimicheskii institut im. N. Ya. Karpova (Physicochemical Institute)

Card 2/3

ACCESSION NR: AP4009150

SUBMITTED: 07Aug62

DATE ACQ: 10Feb64

ENCL: 00

SUB CODE: 00

NO REF SOV: 004

OTHER: 003

Card 3/3

BEREZIN, G.P.; KHOMICHVSKIY, I.M.; MEDVEDEV, S.S.; GOLITSAN, I.V.

Effect of the addition of emulsifying agents on the course of the emulsion polymerization of styrene. Vysokom. soed. 6 no. 5:891-895 My '64. (RUSSIA 17:6)

I. Koskovskiy Institut tekhnologiy tekstil'nykh i khimicheskikh Lomonosova i Khimiko-khimicheskii Institut Inzh. Karpova.

L 16327-65 EWT(m)/EPF(c)/EWP(j)/T PC-4/Pr-4 RM  
 ACCESSION NR: AP4949153 S/0190/64/006/011/2030/2034

AUTHOR: Rozenberg, B. A.; Chekhuta, O. M.; Lyudvig, Ye. B.; Gantmakher, A. R.;  
 Medvedev, S. S.

TITLE: Kinetics and equilibrium of the polymerization of tetrahydrofuran induced by tri-  
 alkylxonium salts

SOURCE: Vy\*sokomolekulyarny\*ye soyedineniya, v. 6, no. 11, 1964, 2030-2034

TOPIC TAGS: trialkylxonium, tetrahydrofuran, block polymerization, solution polymeri-  
 zation, tetrafluoroborate, cationic polymerization

ABSTRACT: The kinetics of the polymerization of tetrahydrofuran, both in block and in  
 solution in diethyl ether, under the influence of triethyloxonium tetrafluoroborate was in-  
 vestigated by a dilatometric method. The characteristics of the catalyst and the initial  
 substances are given. The kinetic curves at different initial catalyst concentrations are  
 given, showing that the rate of polymerization is directly proportional to the concentration  
 of catalyst and is described by the equation  $d[M]/dt = k_p[C_0]([M] - [M_0])$ . The rate con-  
 stant of the polymerization at 20°C determined from the experimental data is equal to  $1.66$   
 $\times 10^{-2}$  liter/mole. sec. A study of the effect of the catalyst concentration on the molecular

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L 16327-65

ACCESSION NR: AP4049158

2

weight of the forming polymer showed that over the concentration range 0.02-0.08 mole/liter the molecular weight is inversely proportional to the catalyst concentration. Tabulated data show that at a constant concentration of catalyst (0.02 mole/liter), the molecular weight increases with increasing amount of polymerized monomer. Over a temperature range of 0-40°C, the rate of polymerization, the equilibrium state and the molecular weight were found to be highly dependent on temperature. From the temperature dependence of the rate constant, the energy of activation was  $E=13.3$  kcal/mole and the preexponential factor  $A=1.64 \times 10^{-8}$  liter/mole. sec. The molecular weight decreased considerably with increasing temperature. The equilibrium concentration of the monomer during polymerization was independent of the initial concentrations of catalyst and monomer and depended only on the temperature. On the basis of this correlation, the change in enthalpy and entropy of polymerization was calculated:  $\Delta H = -5.5$  kcal/mole;  $\Delta S = -20.8$  cal/mole. deg. The limiting temperature of block polymerization calculated by the equation  $T_0 = \Delta H / \Delta S + R \log [M_p]$  is 73°C. Orig. art. has: 6 figures, 1 table and 1 formula.

ASSOCIATION: Donetskoye otdeleniye Instituta organicheskoy khimii AN USSR (Donetsk Division of the Institute of Organic Chemistry, AN Ukr. SSR); Fiziko-khimicheskiy Institut im. L. Ya. Karpova (Institute of Physical Chemistry)

Card 2/8

L 16327-65  
ACCESSION NR: AP4049153

SUBMITTED: 23Jan84

ENCL: 00

SUB CODE: 00

NO REF SOV: 003

OTHER: 018

Card 3/3

L 16326-65 EWI(m)/EPE(c)/EWH(j)/I Pr-4/Pt-4 RM  
 ACCESSION NR: AP4049154 S/0190/64/006/011/2035/2039

AUTHOR: Rozenberg, B. A.; Lyudvig, Ye. B.; Gantmakher, A. R.; Medvedev, S. S. 13

TITLE: Mechanism of the induced polymerization of tetrahydrofuran induced by trialkyloxonium salts

SOURCE: Vy\*sokmolekulyarny\*ye soyedineniya, v. 6, no. 11, 1964, 2035-2039

TOPIC TAGS: tetrahydrofuran, boron fluoride etherate, epichlorohydrin polymerization, living polymer, polytetramethylene oxide, trialkyloxonium salt, tetrahydrofuran polymerization, cationic polymerization

ABSTRACT: The mechanism of the cationic polymerization of tetrahydrofuran was investigated and the peculiarities of the polymerization induced by trialkyloxonium salts were discussed on the basis of the given reaction mechanisms. By the analytical method used, it was found that the initiation of the polymerization of tetrahydrofuran in the presence of the system boron fluoride etherate + epichlorohydrin proceeds with the formation of distinct ion pairs and an internal oxonium salt. The peculiarity of the tetrahydrofuran polymerization is that, in contrast to the cationic polymerization of vinyl compounds, the growing ion is oxonium and not carbon. Infrared spectra show the complete absence of

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L 16326-65

ACCESSION NR: AP4049154

lateral methyl groups in the polytetramethylene oxide molecule. On the basis of an analysis of the experimental data, it was established that the polymerization of tetrahydrofuran induced by trialkyloxonium salts proceeds without the rupture of the reaction chains and with the formation of "living polymers." The effect of small additions of water on the polymerization was also studied and water was found to be the chain transfer agent. Its addition does not affect the rate of polymerization, but decreases the molecular weight. The molecular weight also decreases with increasing temperature of polymerization, but the decrease in molecular weight is determined not by the decrease in the ratio between the rate constant of chain growth and the rate constant of chain rupture, as in the cationic polymerization of unsaturated compounds, but by the decrease in the equilibrium concentration of the monomer with increasing temperature. On the basis of the equilibrium monomer concentration, the rate constant of the reversible reaction was calculated as  $k_d = 4.67 \times 10^{-2} \text{ sec}^{-1}$  (at 20°C). From the temperature dependence of this constant, the activation energy and the preexponential factor of the depolymerization reaction determined from this relationship are  $E=19.4 \text{ kcal/mole}$  and  $A=1.65 \times 10^{13}$ . It was found that the molecular weights of polytetramethylene oxide are in disagreement with the values expected according to the M/C theory. Orig. art. has: 2 figures, 1 table and 12 formulas.

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L 16326-65

ACCESSION NR: AP4049154

ASSOCIATION: Donetskoye otdeleniye instituta organicheskoy khimii AN USSR (Donetsk  
Division of the Institute of Organic Chemistry, AN Ukr. SSR); Fiziko-khimicheskiy institut  
im. L. Ya. Karpova (Institute of Physical Chemistry)

SUBMITTED: 23Jan64

ENCL: 00

SUB CODE: OC

NO REF SOV: 002

OTHER: 012

Card 3/3

TELESHOV, E.N.; PRAVEDNIKOV, A.N.; MEDVEDEV, S.S., akademik

Mechanism of polyisobutylene radiolysis. Dokl. AN SSSR 156 no.6:  
1395-1398 Je '64. (MIRA 17:8)

1. Nauchno-issledovatel'skiy fiziko-khimicheskiy institut imeni  
L.Ya. Karpova.

L 56067-68 SWT(m)/EPP(a)/EWP(j)/T Pg-4/Pr-4 RM

ACCESSION NR: AP5018555

UR/0020/64/158/004/0876/0879

AUTHOR: Basova, R. V.; Gantmakher, A. R.; Medvedev, S. S. (Academician)

TITLE: Influence of the nature of the active sites on processes of anionic and anionic-coordinative polymerization

SOURCE: AN SSSR, Doklady, v. 158, no. 4, 1964, 876-879

TOPIC TAGS: polymerization, organopotassium compound, monomer

Abstract: The influence of the nature of the monomer and the medium on the structure and properties of the active sites in polymerization initiated by organopotassium compounds was studied. The kinetics of the polymerization of alpha-methylstyrene, styrene, isoprene, and butadiene was investigated, both in hydrocarbon medium (benzene, toluene, cumene) and in the presence of additions of tetrahydrofuran (0.5 to 50%) at various temperatures (-50° to +30°), by a dilatometric method, and the molecular weights of the corresponding polymers were determined. Organopotassium compounds synthesized in hydrocarbon medium (1,2) or in tetrahydrofuran medium (3,4) were used in initiators: 1) benzylpotassium; 2) low-molecular dipotassiumpoly-alpha-methylstyrene; 3) potassium naphthalene; 4) dipotassium tetramer of alpha-methylstyrene. The activity of the monomers increased in the sequence: alpha-methylstyrene < isoprene <

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L 56067-65

ACCESSION NR: AP5018555

<butadiene <styrene. The rate of the initiation of polymerization of various monomers in hydrocarbon medium at 0° in the presence of benzylpotassium increased with increasing activity of the monomers in the sequence isoprene <butadiene <styrene; in the case of dipotassium poly-alpha-methylstyrene, a compound with a less stable carbanion, even the polymerization of isoprene took place without an induction period. In the polymerization of alpha-methylstyrene with organopotassium compounds in a mixture of cumene or toluene with tetrahydrofuran (~50%), even at 50°, the molecular weight of poly-alpha-methylstyrene was lower than expected, indicating the presence of a reaction of chain transfer through the monomer. Orig. art. has 1 graph and 1 table.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physicochemical Institute)

SUBMITTED: 25May64

ENCL: 00

SUB CODE: 00, 00

NO REF SOV: 004

OTHER: 001

JPRS

*PR*  
Card 2/2

KIRCHEVSKAYA, I.Yu.; MEDVEDEV, S.S., akademik

Effect of water on the course of butadiene polymerization in the presence  
of complex cobalt catalysts. Dokl. AN SSSR 158 no.5:1116-1119 0 '64.  
(MIRA 17:10)

1. Moskovskiy institut tonkoy khimicheskoy tekhnologii im. M.V.Lomonosova.

I 36632-65 EWI(m)/EPF(c)/EWP(j)/T - Pc-4/Pr-4 RM

ACCESSION NR: AP5001515

S/0020/64/159/005/1066/1068

AUTHOR: Arest-Yakubovich, A. A.; Medvedev, S. S. (Academician)

TITLE: Anionic polymerization of butadiene in tetrahydrofuran

SOURCE: AN SSSR. Doklady, v. 259, no. 5, 1964, 1066-1068

TOPIC TAGS: butadiene, polymerization, tetrahydrofuran, solvation, polymerization initiator, alkali metal, reaction rate

ABSTRACT: A study was made of the polymerization kinetics of butadiene in tetrahydrofuran (THF) in the presence of alkali metal complexes with biphenyl in a broad temperature interval. In the majority of cases measurements were carried out dilatometrically. The kinetics of the most rapid processes which occur in the presence of potassium and cesium initiators at -30C and higher were investigated by determining the yield of the polymer in a definite period of time in a thermostated reactor with a high speed stirrer. The change of the rate of reaction with time is described well by the first order equation with respect to the

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L 36632-65

ACCESSION NR: AP5001515

monomer. At  $-96^{\circ}\text{C}$  the rate of reaction is directly proportional to the concentration of the initiator within  $2 \cdot 10^{-3}$  -  $3 \cdot 10^{-2}$  mole/l limits. It was found that the rate of polymerization and the structure of polybutadiene depends on the nature of the counter ion. The preliminary data indicate that the use of solvent with even greater solvation ability than THF, such as dimethoxyethane, leads to a significant increase of the rate of sodium initiated polymerization of butadiene. The authors wish to express their gratitude to A. R. Gantmakher for his interest in this work and discussion of the results and to N. V. Desyatova for the determination of the microstructure of polybutadiene by the infrared spectroscopy method. Orig. art. has: 2 tables and 2 figures

ASSOCIATION: Fiziko-Khimicheskiy Institut Im. L. Ya. Karpova (Institute of Physical Chemistry)

SUBMITTED: 13Jul64

ENCL: 00

SUB CODE: ME, GC

NR REF SOV: 005

OTHER: 002

Card 2/2

POLYAKOV, D.A., LITVINENKO, V.M., LITVINENKO, V.M.

Effect of the concentration of the compounds on their  
ultraviolet spectra. Spectrochim. Acta 18:5, 1965.

(MIRA 18:5)



ROZENBERG, B.A.; LYUDVIG, Ye.B.; GANTMAKHER, A.R.; MEDVEDEV, S.S.

Effect of reaction chain transfer to polymer in the cationic  
polymerization of oxygen-containing cyclic compounds. *Vysokom.*  
soed. 7 no.1:188-189 Ja '65. (MIRA 18:5)

LYUFVIG, Ye.B.; ROZENBERG, B.A.; ZVEREVA, T.D.; GANTMAN, A.S.;  
MEVEDEV, S.S.

Polymerization of tetrahydrofuran in the presence of antimony  
pentachloride and its compounds. *Vysokom. soed.* no.2:269-274  
F 165. (1974, 18:3)

1. Fiziko-khimicheskiy institut im. N. S. Kurnakova, Moskva i Donetskii  
filial Instituta khimicheskikh reaktivov i osobennostykh veshchestv.

STAVROVA, S.D.; MARGARITOVA, M.F.; MEDVEDEV, S.S.

Emulsion polymerization kinetics of methyl methacrylate  
in the presence of organic acids and amines and  $\alpha$  cation-  
active emulsifier. Vysokom. soed. " no.4:717-724 Ap '65.  
(MIRA 18:6)

1. Moskovskiy institut tonkoy khimicheskoy tekhnologii imeni  
Lomonosova.

LANOVSKAYA, L.M.; MAKLETSOVA, N.V. [deceased]; GANTMAKHER, A.R.;  
MEDVEDEV, S.S.

Polymerization of ethylene in the presence of various composite catalysts based on  $TiCl_3$ . Vysokom. soed. 7 no.4:741-746 Ad '65.

Nature of the active centers in the processes of polymerization in the presence of composite catalysts based on  $TiCl_3$ . Ibid.: 747-750

(MIRA 18:6)

1. Fiziko-khimicheskiy institut imeni Karpova, Moskva.

ROZENBERG, B.A.; LYUDVIG, Ye.B.; DESYATOVA, N.V.; GNATMAKHER, A.R.; MEDVEDEV, S.S.

Copolymerization of tetrahydrofuran with  $\alpha$ -oxides. Vysokom. soed. 7 no.6:  
101C-1015 Je '65. (MIRA 18:9)

1. Fiziko-khimicheskiy institut imeni L.Ya.Karpova, Moskva.

KRISTAL'NYY, E.V.; MEDVEDEV, S.S.

$\gamma$ -ray-induced polymerization of isobutylene in the presence  
of ZnO and Al<sub>2</sub>O<sub>3</sub>. Vysokom. soed. 7 no.8:1373-1376 Ag '65.  
(MIRA 18:9)

1. Fiziko-khimicheskiy institut imeni L.Ya.Karpova AN SSSR,  
Moskva.

TRUBITSYNA S.N.; MARGARITOVA, M.F.; MEDVEDEV, S.S.

Emulsion polymerization of methyl methacrylate in the presence  
of benzoyl peroxide at low temperatures. Vysokom. soed. 7 no.11:  
1973-1977 N '65. (MIRA 19:1)

1. Moskovskiy institut tonkoy khimicheskoy tekhnologii imeni  
M.V. Lomonosova. Submitted December 26, 1964.

L 27305-66 EWT(m)/ENP(j)/I IJP(c) RM

ACC NR: AP6008981

(A)

SOURCE CODE: UR/0190/65/007/011/1968/1972

AUTHORS: Trubitsyna, S. N.; Margaritova, M. F.; Medvedev, S. S.

ORG: Moscow Institute of Fine Chemical Technology im. M. V. Lomonosov  
(Moskovskiy institut tonkoy khimicheskoy tekhnologii)

TITLE: Investigation of polymerization initiation by the system benzoyl peroxide-alkylpyridinium in alkali media

SOURCE: Vysokomolekulyarnyye soyedineniya, v. 7, no. 11, 1965, 1968-1972

TOPIC TAGS: radical polymerization, emulsion polymerization, chloroprene, benzoyl peroxide, monomer, vinyl, chloroprene, isoprene, butadiene, polymer

ABSTRACT: This investigation was conducted to extend earlier published work by M. F. Margaritova and S. D. Yevstratova (Vysokomolek. soyed., 3, 398, 1961) and to study the role played by cetylpyridinium chloride and cetylpyridinium bromide in initiation of polymerization. The study was carried out by observing the rate of benzoyl peroxide decomposition in the presence of alkylpyridiniums in benzene-water emulsions at 20-22C. The experimental results are presented in graphs and tables. The polymerization of a number of vinyl and diene monomers (methyl-

Card 1/3

UDC: 66.095.26

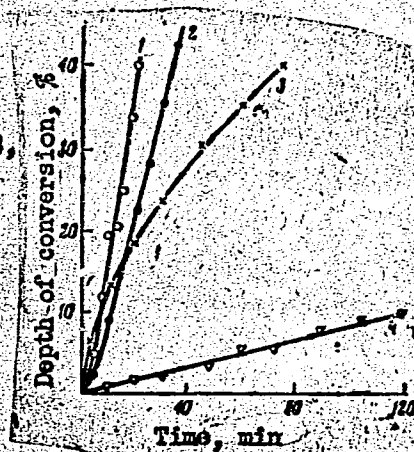


L 27305-66

ACC NR: AP6008981

methacrylate, styrene, chloroprene, isoprene, butadiene) in the presence of benzoyl peroxide--cetylpyridinium chloride was also studied. It was found that acrylonitrile and methacrylate did not polymerize under these conditions. The experimental results are presented graphically (see Fig. 1).

Fig. 1. Polymerization of monomers in the presence of the system—benzoyl peroxide—cetylpyridinium chloride: benzoyl peroxide = 0.745 mole/liter, cetylpyridinium chloride = 2%, pH ~ 10.3, T = 20°C. 1—chloroprene, 2—methylmethacrylate, 3—styrene, 4—isooprene.



Card 2/3

L 27305-66

ACC NR: AP6008931

The order of the initiation reaction for each component and the activation energy for the reaction were determined. The inhibiting effect of benzoic acid on the decomposition of benzoyl peroxide and the polymerization of the monomers was established. It is suggested that a chemical interaction takes place between benzoyl peroxide and acryl pyridiniums in alkali media. Orig. art. has: 1 table and 4 graphs.

SUB CODE: 11/ SUBM DATE: 26Dec64/ ORIG REF: 003/ OTH REF: 001

Card 3/3

L 27306-66 EWT(m)/EWP(j)/T IJP(c) 114/RM  
 ACC NR: AP6008982 (P) SOURCE CODE: UR/0190/65/007/011/1975/1977

AUTHORS: Trubitsyna, S. N.; Margaritova, M. F.; Medvedev, S. S. 27

ORG: Moscow Institute of Fine Chemical Technology im. M. V. Lomonosov (Moskovskiy institut tonkoy khimicheskoy tekhnologii) B

TITLE: Emulsion polymerization of methylmethacrylate in the presence of benzoyl peroxide at low temperatures

SOURCE: Vysokomolekulyarnyye soyedineniya, v. 7, no. 11, 1965, 1973-1977

TOPIC TAGS: emulsion polymerization, polymerization kinetics, methylmethacrylate

ABSTRACT: This investigation was performed to extend an earlier work of M. F. Margaritova and S. D. Yevstratova (Vysokomolek. soyed., 3, 390, 1961). It was desired to determine the effect of initiator and emulsifier system concentration, pH of the medium, and the temperature on the emulsion polymerization of methylmethacrylate. The initiator systems used were benzoyl peroxide--dimethyl aniline and benzoyl peroxide--cetylpyridinium chloride. The latter also served as the emulsifying agent. The experimental results are presented in graphs and tables (see Fig. 1). Rate expressions for the polymerization reactions have been derived. A comparison of the molecular weights of the polymers obtained from the two different initiating systems showed that dimethylaniline decreases the molecular weight by two orders of magnitude. It is concluded that the decrease in molecular weight is caused by the inhibiting action of

Card 1/2 UDC: 66.995.26+678.744 2

L 27306-66

ACC NR: AP6008982

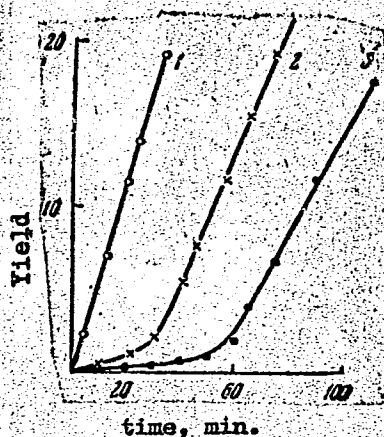


Fig. 1. Polymerization of methylmethacrylate under the influence of the initiating system benzoyl peroxide--cetylpyridinium chloride for different monomer concentrations. Benzoyl peroxide concentration = cetylpyridinium chloride concentration = 0.0745 mole/liter, T = 20°C, pH ~ 10.5. Ratio of organic to aqueous phase: 1 - 1:1; 2 - 1:2; 3 - 1:4.

the reaction products resulting from the reaction of benzoyl peroxide and dimethyl-aniline (chiefly, monomethyl aniline). Orig. art. has: 1 table and 5 graphs.

SUB CODE: 07, 11/SUBM DATE: 26Dec64/ ORIG REF: 006/ OTH REF: 002

Card 2/2

PRONINA, I.A.; SPIRIN, Yu.L.; BLAGONRAVOVA, A.A.; AREF'YEVA, S.M.; GANTMAKHER, A.R.; MEDVEDEV, S.S., akademik

Mechanism underlying the catalytic action of  $\text{Co}^{2+}$  compounds in the urethane-forming reaction. Dokl. AN SSSR 161 no.2:362-365 Mr '65. (MIRA 18:4)

1. Gosudarstvennyy nauchno-issledovatel'skiy i proyektnyy institut lakokrasochnoy promyshlennosti i Fiziko-khimicheskiy institut im. L.Ya.Karpova.

L 53757-65 LRI(I)/LRI(M)/LPI(C)/LPA(W)-2/LWP(J)/T/EWA(E)-2 PC-4/PAB-10/

PR-4 LWP(C) RM

ACCESSION NR: AP5010172

UR/0020/65/161/002/0406/0409

AUTHOR: Shigorin, D. N.; Medvedev, S. S.; Potapov, V. K.

TITLE: Role of  $n\pi^*$  transitions in the processes of the ionization and decomposition of compounds

SOURCE: AN SSSR. Doklady, v. 161, no. 2, 1965, 406-409

TOPIC TAGS: electron transition, ionization curve, anthraquinone molecule, fluorenone molecule, cation radical, mass spectrographic analysis, carbonyl group, chromophoric group /MKh-1303 mass spectrometer/

ABSTRACT: With the aim of elucidating the role of  $n\pi^*$  transitions in the processes of the ionization and decomposition of molecules, the author investigated the ionization curves and occurrence potentials of ions of anthraquinone and fluorenone by the electron shock method. The investigations were performed with the aid of a MKh-1303 high-resolution chemical mass-spectrometer adapted to measuring the ionization potentials of molecules by the electron quasimonokinization method. The first ionization potentials of the molecules of anthraquinone and fluorenone correspond to the energies of

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L 53757-65

ACCESSION NR: AP501/172

separation of electrons from an undivided pair of oxygen atoms, while the second potentials correspond to the separation energies of  $\pi$ -electrons. This conclusion is in agreement with the fact that the first longwave band of the absorption spectrum of the anthraquinone molecule corresponds to the  $\pi \rightarrow \pi^*$  electron transition and the second band, to the  $n \rightarrow \pi^*$  electron transition. For fluorenone the yield of ions formed by the separation of the  $n$ -electron from a pair of oxygen electrons is 2-3 times smaller than for anthraquinone. This may be related to the difference in their ionization potentials ( $I_{\pi} - I_n$ ) and the number of  $\pi$ -electrons of the investigated molecules per chromophoric group. The principal processes of the decomposition of anthraquinone molecules, as indicated by mass-spectrographic analysis, are the processes of the isolation of neutral CO groups from the molecules and formation of  $C_6H_4COC_6H_4^+$  and  $C_6H_4C_6H_4^+$  ions. Their occurrence potentials, as well as the occurrence potentials of the  $C_6H_4C_6H_4^+$  ion from fluorenone, are tabulated. It is assumed that during the decomposition of the anthraquinone molecule and absorption of an energy of 10.39 ev by that molecule a single CO group is released. In the event of the absorption of an energy of 11.02 ev, two carbonyl groups are successively split off that molecule. One group is released by fluorenone at 10.14 ev. In both cases there form ions of

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L 53757-65

ACCESSION NR: AP5010172

an identical structure corresponding to the cation-radical of o-diphenylene. This may account, e.g., for the mechanism of the decomposition of alcohols. The molecules of these compounds, when in specified states, decompose as a result of the exchange interaction between the unpaired electrons of the oxygen atom and the electron of the adjacent carbon atom, which leads to the formation of a new bond between carbon and oxygen and the disruption of the C-H or C-C bond and the concomitant formation of the corresponding radicals  $R\text{-CH}\cdot\text{OH}$  and cations  $R\text{-HC}^+ = \text{O}\cdot\text{H}$ . Orig. art. has: 5 figures, 1 table.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (L. Ya. Karpov Physicochemical Institute)

SUBMITTED: 31Aug64

ENC: 00

SUB CODE: OC, GC

NO REF SOV: 008

OTHER: 003

484  
Card 3/3



KIRCHEVSKAYA, I.Yu.; VOLKOV, L.A.; TIMOFFEYeva, G.V.; MEDVEDEV, S.S., akademik

Stationary and nonstationary processes of butadiene polymerization  
catalyzed by the system  $R_2AlCl - CoCl_2(Py)_2$ . Dokl. AN SSSR 163 no.2:  
375-378 J1 '65. (MIRA 18:7)

1. Mankovskiy institut tonkoy khimicheskoy tekhnologii im. M.V.  
Lomonosova.

STAVROVA, D.S.; MARGARITOVA, M.F.; MEDVEDEV, S.S.; Prinsipala uchastiye  
GOL'SHTEYN, S.B.

Emulsion polymerization kinetics of methyl methacrylate in the  
presence of organic acids and amines and an anion-active emul-  
sifier. Vysokom. soed. 7 no.4:725-728 Ap '65. (MIRA 18:6)

1. Moskovskiy institut tonkoy khimicheskoy tekhnologii imeni  
Lomonosova.

KRISTAL'NYY, E.V.; MEDVEDEV, S.S.

*$\gamma$* -ray-induced polymerization of isobutylene in the presence  
of solids. Vysokom. soed. 7 no.8:1377-1382 Ag '65. (MIRA 18:9)

1. Fiziko-khimicheskiy institut imeni L.Ya.Karpova AN SSSR,  
Moskva.

L 27116-66 ENT(m)/ENP(j)/T IJP(c) RM

ACC NR: AP6012713

(A)

SOURCE CODE: UR/0190/66/008/004/0681/0685

AUTHOR: Arest-Yakubovich, A. A.; Medvedev, S. S.

ORG: Physicochemical Institute im. L. Ya. Karpov (Fiziko-khimicheskiy institut im. L. Ya. Karpova)

TITLE: Effect of the nature of counter ions and the medium in anionic polymerization of butadiene

SOURCE: Vysokomolekulyarnyye soyedineniya, v. 8, no. 4, 1966, 681-685

TOPIC TAGS: butadiene, polymer, polymerization kinetics, polymerization rate, polymer structure, counter ion

ABSTRACT: The basic factors determining the kinetics of butadiene polymerization in electron-donor compounds and the microstructure of the polymer were investigated. It was found that the polymerization rate greatly depends on the nature of the counter ion and the solvent. The polymerization rate sharply increases in the series lithium < sodium < potassium at temperatures above -60C. The polymerization rate is also greatly increased during the transition from tetrahydrofuran to dimethoxyethane. During a gradual change in the composition of the tetrahydrofuran and dimethoxyethane solvent, the polymerization rate is linearly changed without a sharp increase in the range of low dimethoxyethane concentrations. The polymer microstructure greatly depends on the reaction temperature of polymerization and on the nature of the counter-

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ion. The authors thank A. R. Gantmakher for his interest in this work and fruitful discussions of the results. Orig. art. has: 2 figures and 2 tables. [NT]

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Card 2/2 BK

KRAKHT, S.V.; MEDEDEV, S.V.; KOZ'MINSKAYA, Ye.I.

On the problems of outbreaks of tonsillitis. Voen.-med. zhur. no.9:  
57-60 S '51. (MIRA 9:9)  
(THROAT--DISEASES)

MEDVEDEV S.V.

3  
IRML

V 7809

INDUSTRIAL GAMMA-DEFECTOSCOPY L. K. Tskchenko  
and S. V. Medvedev. Moscow, Metallurgizdat, 1955. (In  
Russian) (Book on display at Geneva Conference)

A manual for industrial examination of metallic articles  
by  $\gamma$  rays from radioactive cobalt and iridium isotopes.  
Description of equipment employed in defectoscopy in the  
photographic and ionization methods. Methods of dosimetry  
of  $\gamma$  radiation; experience in the use of  $\gamma$  defectoscopy at  
the plant; organization of labor in  $\gamma$  defectoscopy and safety  
engineering. (publisher's note)

RMZ

①

RMZ

MEDVEDEV, S. V., TATOCHENKO, L. K. and TOKMAKOV, V. S.

"Application of radio active iridium for gamma defect detection", appearing in the "Detection of Defects in Metals by Gamma — Collection of Papers", (Gamma Defektoskopiya Metallov — Sbornik Statei), published by the Academy of Sciences USSR, p 94, 1955.



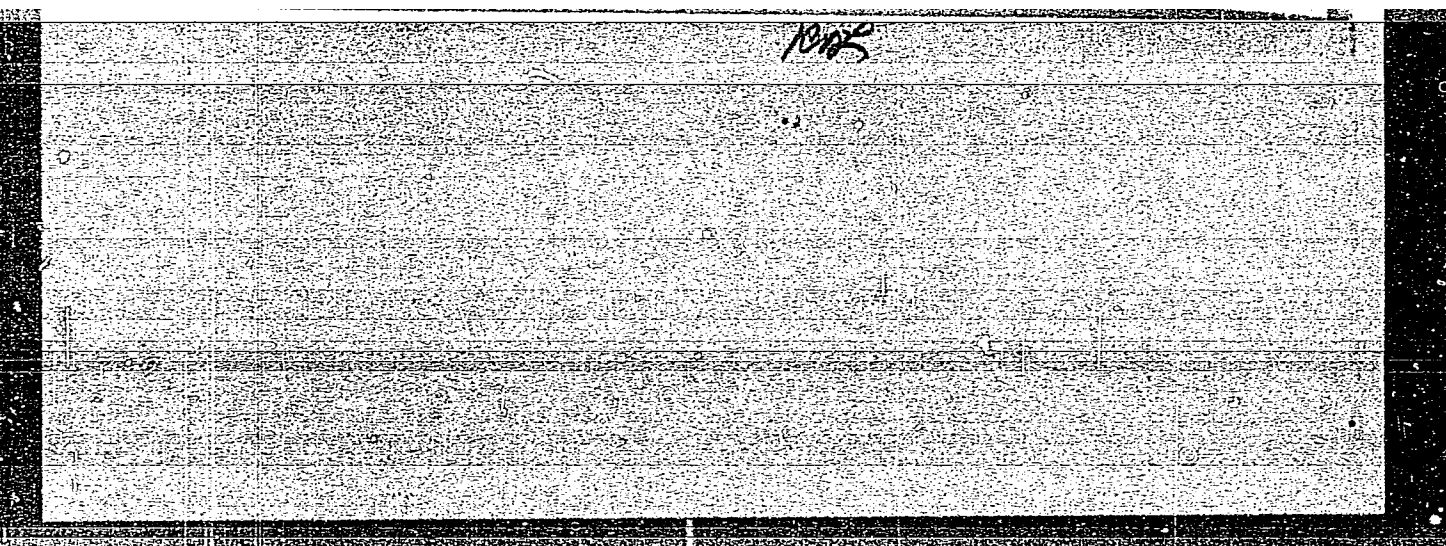
19

*Medvedev, S. K.*

Des. of Radiactive Indicators for Measuring Liquid Levels.  
by S. K. Medvedev and A. V. Medvedev. (Radiatsiya Labora-  
toriya, 1965, 21, (10), 1125-1127, 11n Russian). Descriptions  
are given of apparatus developed in the U.S.S.R. for the  
determination of the levels of fused metals and other liquids  
with the aid of radioactive isotopes. The types suitable for  
liquid metal level indication are IU-2, IU-2a, and IU-3.  
The first two are indicators, and the IU-3 instruments can be  
used for automatic recording and level control. All are of  
the gamma-ray type, the source being  $^{60}\text{Co}$ . Halogen counters  
are used with all except the IU-2,--s. g.

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APPROVED FOR RELEASE: 07/12/2001

CIA-RDP86-00513R001033310003-7"

MEDVEDEV, S.V.; LATYSHEV, V.K.

New methods for fluid level measuring using radioactive isotopes.  
Priborostroenie no.8:6-9 Ag '56. (MLRA 9:10)

(Radioactive tracers--Industrial applications)  
(Measuring instruments)

MEDVEDEV, S. V.

On the consequences of the Carpathian Earthquake of 1940. Trudy Geofizich  
Instituta of the USSR Academy of Sciences. No 1, 1949. (?)